

# PATENT SPECIFICATION

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(19)



## (54) A METHOD FOR OBTAINING HIGHER TiO<sub>2</sub> GRADE ANATASE CONCENTRATES FROM LOWER TiO<sub>2</sub> GRADE ANATASE CONCENTRATES

(71) We, MINERACÃO VALE DO PARANAÍBA S.A.—VALEP, a Brazilian Company of Rua Marquês de Maricá Nº 181, Belo Horizonte, Minas Gerais, Brazil, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a chemical up-grading process for lower TiO<sub>2</sub> grade anatase concentrates which makes it possible to obtain therefrom higher TiO<sub>2</sub> grade anatase concentrates having chemical properties very similar to those of naturally occurring rutile ore, and containing a high percentage of titanium dioxide (TiO<sub>2</sub>) and only a small content of iron.

Titanium, which is one of the most abundant elements in the earth's crust, has hitherto been found to occur naturally in only two mineral forms of commercial importance, namely rutile and ilmenite. Rutile ore, when pure, consists basically of titanium dioxide (about 96% by weight), with very small percentages of iron. Ilmenite, which is essentially a ferrous titanate (FeO. TiO<sub>2</sub>), theoretically has a TiO<sub>2</sub> content of 52.66% by weight. This value, however, may vary between 40 and 60% in commercially available products, depending mainly on the relative percentages of ferrous iron and ferric iron. This great variation in the titanium dioxide content of ilmenite is due to the presence of other mineral elements in the ilmenite lattice, in the case of the lower grade materials, and to dissociation of the iron oxides by weathering, in the case of higher TiO<sub>2</sub> grade materials.

Titanium concentrates are used in the production of both pigments and titanium metal. Titanium metal is light and resistant to corrosion. It is widely used in the aeronautic, aerospace, and chemical industries. It is also applied in sea water desalination plants, in cryogenics, and in oceanography. Titanium dioxide, on the other hand, is the basic pigment used in paint manufacture, and is also widely used in the paper and plastics industries.

The demand for rutile has greatly increased in recent years due to its growing use in pigment production. Because of its very high TiO<sub>2</sub> content, pigments can be produced from it with only minor pollution problems. For this reason, rutile has become an expensive ore, and currently known world deposits are limited.

The recent discoveries of large bodies of anatase in complex association with other minerals in vertical veins of ore of volcanic origin in the Brazilian states of Minas Gerais and Goiás, have opened up very promising prospects for the titanium raw material industry in Brazil. However, the anatase ore recently found is quite different from other known titaniferous ores, and it occurs in association with other TiO<sub>2</sub> minerals such as ilmenite (FeO. TiO<sub>2</sub>), perovskite (Ca.TiO<sub>3</sub>), and titaniferous magnetite.

After being mined, the anatase ore is subjected to mechanical beneficiation resulting in concentrates with TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> contents of between 70% and 80% by weight and between 8% and 15% by weight respectively.

The following is a typical analysis of an anatase concentrate thus obtained, the percentages being by weight:—

$\text{TiO}_2 = 78.12\%$        $\text{MgO} = 0.84\%$

$\text{Fe}_2\text{O}_3 = 1.09\%$        $\text{CaO} = 0.70\%$

$\text{SiO}_2 = 1.09\%$        $\text{Mn}_2\text{O}_3 = 0.67\%$

$\text{P}_2\text{O}_5 = 1.74\%$        $\text{L.I.} = 1.85\%$

5       $\text{Al}_2\text{O}_3 = 1.04\%$

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It is an object of the present invention to provide a method of upgrading the above-mentioned concentrates to a very high-grade product, similar in nature to rutile and having a high  $\text{TiO}_2$  content and a low  $\text{Fe}_2\text{O}_3$  content.

10      According to the invention, there is provided a method of producing a higher  $\text{TiO}_2$  grade anatase concentrate from a lower grade concentrate which comprises the steps of subjecting the lower grade concentrate to a reducing treatment in the presence of gaseous  $\text{SO}_2$  and/or  $\text{H}_2\text{S}$  at elevated temperature, leaching the reduction product with mineral acid, and subjecting the leached product to magnetic separation, the non-magnetic fraction being withdrawn as the desired higher grade concentrate.

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15      The reduction step in the presence of gaseous  $\text{SO}_2$  and/or  $\text{H}_2\text{S}$ , may be carried out at a temperature of, for example, 500 to 1300°C. The hydrogen sulphide gas given off in the acid leaching step may be recycled to the reduction step. The acid leaching step may be carried out at a temperature between ambient temperature and the boiling point of the acid used.

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20      The magnetic separation step may be carried out in a magnetic field having a strength of between 7000 and 25000 gauss. If desired, the magnetic fraction separated in this step may be recycled to the reduction step.

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25      If desired, the acid-leached material may be subjected to alkaline leaching to reduce the phosphorus and aluminium contents.

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30      In a preferred embodiment of the invention, the mechanically obtained anatase concentrate is initially reduced in the presence of  $\text{SO}_2$  (sulphur dioxide gas) and/or  $\text{H}_2\text{S}$  (hydrogen sulphide gas) in a rotary kiln or any other type of kiln which permits a good gas/solid contact between the reducing gas and the concentrate. The reducing gas mixture is produced by the combustion of gases in conventional burners. The reduction is effected at a temperature in the range of 500 to 1300°C. In addition to reducing the ore, the gaseous mixture opens up the crystal lattice of the impure titaniferous ore, thus allowing the iron and other metallic ions to react and form sulphides such as iron sulphides, magnesium sulphides, and the like.

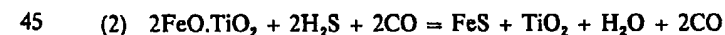
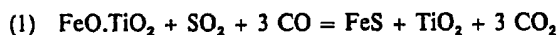
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35      After reduction, the material is cooled in a reducing or protective atmosphere to avoid reoxidation of the reduced material. It is then treated with a mineral acid solution, such as hydrochloric acid and/or sulphuric acid, at temperatures ranging from room temperature to the boiling point of the acid solution. The optimum concentration for the acids is usually from 10 to 20% for hydrochloric acid and from 20 to 30% for sulphuric acid, but other concentrations may be used. At this point, the metal sulphides formed and other impurities are leached by the action of the acid.

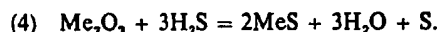
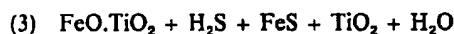
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40      The main chemical reaction involved in the process are as follows:—

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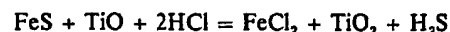


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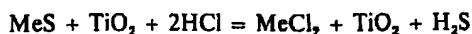


50      Iron sulphide (FeS) produced in any of reactions (1), (2) and (3) is leached in acid solution, which results in the formation of hydrogen sulphide ( $\text{H}_2\text{S}$ ), which is recovered and recycled in the system, thereby reigniting the operational cycle. The chemical reactions involved in this leaching operation can be represented as follows:—

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The other impurities in the original mechanical concentrate of lower  $\text{TiO}_2$  content are also eliminated by leaching with acid solution. The equations for the chemical reactions are as follows (Me representing an impurity metal):—



After the acid treatment, the material is filtered, washed with water, and then submitted to magnetic separation with a high field intensity. Any remaining magnetic materials are recycled, and the final non-magnetic product obtained is the required high  $\text{TiO}_2$  grade anatase concentrate. Its composition includes a minimum  $\text{TiO}_2$  content of 94% by weight and a maximum  $\text{Fe}_2\text{O}_3$  content of 2% by weight, and it has characteristics similar to those of natural rutile.

Where lower phosphorus and aluminium contents are required, these can be further reduced by an additional treatment, after the acid leaching, with sodium hydroxide solutions in concentrations of up to 20% by weight, at temperatures ranging from room temperature to the boiling point of the alkaline solution, depending on the specific nature of the material being treated.

The invention is illustrated by the following non-limitative experiments:—

#### EXPERIMENTAL CONDITIONS

a) **SULPHIDISATION** — 25 g of a low-grade anatase concentrate with an average particle size less than 80 mesh (Tyler Specification) were placed in a quartz tube which was put in a fixed bed furnace heated by an electric resistor. After the furnace temperature had attained the prescribed level, hydrogen sulphide gas ( $\text{H}_2\text{S}$ ) or sulphur dioxide was passed through the tube at a gas flow rate of 240 ml/min. The reactor tube was rotated every five minutes by a manually-driven device in order to mix and expose more of the solids surface to the passing gas. At the end of the sulphidisation process, the sulphidised material was cooled in a non-oxidising atmosphere by passing an inert gas such as argon or nitrogen, thereby preventing reoxidation. These conditions were kept constant during the tests which were carried out to determine the influences of sulphidisation temperature and reaction time.

b) **ACID LEACHING** — 20 g of the sulphidised material were leached with 50 ml of aqueous hydrochloric acid solution having a concentration of 20% by weight (200 g of HCl per litre of solution) for 3 hours under reflux. After leaching, the material was filtered and washed until all residual HCl had been washed away.

c) **MAGNETIC SEPARATION** — The solid material from the acid leaching step was submitted to wet magnetic separation with a high field intensity, resulting in two fractions, one magnetic and the other non-magnetic.

The conditions described above for sulphidisation, acid leaching, sulphidisation temperature and reaction time were studied. The results obtained are given in the following Tables, in which all percentages are by weight.

#### EXPERIMENTAL RESULTS

a) Influence of sulphidisation temperature: material balance and chemical analysis (sulphidisation time was kept at 45 minutes for all runs).

TABLE 1

Sulphidisation Time	Non-magnetic fraction		Magnetic fraction		In solution	
	g	(%)	g	(%)	g	(%)
600°C	14.72	73.60	2.71	13.55	2.57	12.85
700°C	14.70	75.50	2.52	12.60	2.78	13.90
800°C	15.35	76.75	1.50	7.50	3.15	15.75
900°C	15.65	78.25	1.09	5.45	3.26	16.13
1000°C	16.10	80.50	0.60	3.00	3.30	16.50

## SULPHIDISATION

Temperature	600°C	700°C	800°C	900°C	1000°C
TiO <sub>2</sub> %	93.00	94.25	93.2	93.75	94.25
Fe <sub>2</sub> O <sub>3</sub> %	1.70	1.21	0.67	0.56	0.34
SiO <sub>2</sub> %	0.64	0.64	0.86	0.64	0.50
CaO %	0.08	0.07	0.08	0.09	0.09
P <sub>2</sub> O <sub>5</sub> %	1.05	1.02	0.94	1.20	1.12
Al <sub>2</sub> O <sub>3</sub> %	1.11	1.27	1.34	1.32	1.28
MgO %	0.32	0.46	0.50	0.70	0.81

b) Influence of sulphidisation reaction time: (Sulphidisation temperature was kept at 1,000°C).

TABLE II

Sulphidisation Time	Non-Magnetic fraction		Magnetic fraction		In Solution	
	(g)	(%)	(g)	(%)	(g)	(%)
15 mins	15.75	78.75	1.11	5.55	3.14	15.70
30 mins	16.00	60.00	0.60	3.25	3.25	16.75
45 mins	15.90	79.50	0.70	3.50	3.40	17.00
60 mins	15.52	77.60	0.54	2.70	3.94	19.70
90 mins	15.55	77.75	0.86	3.30	3.79	18.95
120 mins	15.50	77.50	0.50	2.50	4.00	20.00

In addition to the factors indicated above, the acid leaching reaction time was also investigated. For these tests, the sulphidisation temperature was kept at 1000°C and the sulphidisation time at 60 mins, with magnetic separation with a high field intensity.

- c) Influence of leaching reaction time: material balance and chemical analysis (sulphidisation temperature: 1000°C; sulphidisation time 60 mins).

TABLE III

Acid Leaching time	Non-Magnetic fraction		Magnetic fraction		In Solution	
	(g)	(%)	(g)	(%)	(g)	(%)
1 hour	16.80	84.00	0.36	1.80	2.84	14.20
2 hours	16.50	82.50	0.40	2.00	3.10	15.50
4 hours	16.04	80.20	0.39	1.95	3.57	17.85
6 hours	16.20	81.00	0.28	1.40	3.52	17.60

TABLE IIIA

Acid Leaching Time	TiO <sub>2</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	SiO <sub>2</sub> %	CaO %	P <sub>2</sub> O <sub>5</sub> %	Al <sub>2</sub> O <sub>3</sub> %	MgO %
1 hour	97.25	0.21	0.30	0.11	0.98	1.04	0.80
2 hours	96.80	0.19	0.22	0.10	0.52	1.02	0.80
4 hours	97.25	0.19	0.26	0.05	0.53	0.94	0.78
6 hours	97.50	0.17	0.40	0.07	0.33	1.02	0.91

On an industrial scale, the process can be described as follows. Low-grade anatase concentrate is fed into a furnace heated directly by combustible gas burning in a conventional burner with a neutral or slightly reducing flame. The sulphidising agent is fed into the furnace, together with the anatase, in excess of the amount required by the stoichiometric reaction. The sulphidised material passes through a cooling device and is directly discharged into the acid leaching system, continuously and in counter-current. The gases from this treatment, which basically consist of H<sub>2</sub>S (hydrogen sulphide gas) are collected and, together with the excess reactant from the sulphidisation furnace, are recycled to the sulphidisation step. The leached material is filtered and submitted to wet magnetic separation with a high field intensity. The magnetic fraction is recycled to the sulphidisation furnace. The non-magnetic fraction produced is the required high TiO<sub>2</sub> grade anatase concentrate.

#### WHAT WE CLAIM IS:—

1. A method of producing a higher TiO<sub>2</sub> grade anatase concentrate from a lower grade concentrate which comprises the steps of subjecting the lower grade concentrate to a reducing treatment in the presence of gaseous SO<sub>2</sub> and/or H<sub>2</sub>S, at elevated temperature leaching the reduction product with mineral acid, and

subjecting the leached product to magnetic separation, the non-magnetic fraction being withdrawn as the desired higher grade concentrate.

2. A method as claimed in Claim 1, wherein the magnetic fraction produced in the magnetic separation step is recycled to the reduction step.

5 3. A method as claimed in Claim 1 or Claim 2, wherein said reduction step is carried out at a temperature in the range of 500 to 1300°C. 5

4. A method as claimed in any one of the preceding Claims, wherein hydrogen sulphide gas given off in the acid leaching step is recycled to the reduction step.

10 5. A method as claimed in any one of the preceding Claims, wherein the acid leaching step is carried out at a temperature between ambient temperature and the boiling point of the acid. 10

6. A method as claimed in any one of the preceding Claims, wherein the leached material is submitted to magnetic separation in a magnetic field of strength between 7000 and 25000 gauss.

15 7. A method as claimed in any one of the preceding Claims, wherein the acid-leached material is subjected to alkaline leaching prior to magnetic separation. 15

8. A method as claimed in Claim 1, of producing a higher  $\text{TiO}_2$  grade anatase concentrate from a lower grade concentrate substantially as hereinbefore described and exemplified.

20 9. A higher  $\text{TiO}_2$  grade anatase concentrate produced from a lower grade concentrate by a method as claimed in any one of the preceding Claims. 20

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